# REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188



| 1. REPORT DATE (DD-MM-YYYY) | 2. REPORT TYPE | 3. DATES COVERED (From - To) |
|---|---|---|
| 29-11-2018 | Final Report | 1-Aug-2016 - 31-Jul-2018 |

4. TITLE AND SUBTITLE

Final Report: HBCU/MI Acquisition of UV/Vis/Raman Spectroscopy and Imaging Instrumentation for Physics and Engineering Research

5a. CONTRACT NUMBER

W911NF-16-1-0427

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

106012

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

University of California - Santa Barbara
3227 Cheadle Hall
3rd floor, MC 2050
Santa Barbara, CA 93106 -2050

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)

ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

68914-PH-REP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | Andrea Young |
| UU | UU | UU | UU | | 19b. TELEPHONE NUMBER |
| | | | | | 805-893-5465 |

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

# RPPR Final Report
as of 11-Feb-2019

Agency Code:

Proposal Number: 68914PHREP **Agreement Number: W911NF-16-1-0427**

**INVESTIGATOR(S):**


**Name:** Andrea Young
**Email:** andrea@physics.ucsb.edu
**Phone Number:** 8058935465
**Principal:** Y

**Name:** Michael J Gordon
**Email:** mjgordon@engineering.ucsb.edu
**Phone Number:** 8058937346
**Principal:** N

Organization: **University of California - Santa Barbara**
Address: 3227 Cheadle Hall, Santa Barbara, CA 931062050
Country: USA

DUNS Number: 094878394 EIN: 956006145W
**Report Date:** 31-Oct-2018 Date Received: 29-Nov-2018
**Final Report** for Period Beginning 01-Aug-2016 and Ending 31-Jul-2018
**Title:** HBCU/MI Acquisition of UV/Vis/Raman Spectroscopy and Imaging Instrumentation for Physics and Engineering Research
**Begin Performance Period:** 01-Aug-2016 **End Performance Period:** 31-Jul-2018
**Report Term:** 0-Other
Submitted By: Andrea Young Email: andrea@physics.ucsb.edu
Phone: (805) 893-5465
**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** **STEM Participants:**

**Major Goals:** The major goals of this instrumentation developement proposal were to purchase parts for and integrate a UV/Vis/Raman spectroscopy and imaging instrument for chemical and structural characterization of materials. UCSB is both a major research university and Hispanic Serving Institution, providing a unique opportunity to leverage a well-developed infrastructure to expand minority access to cutting-edge instrumentation while simultaneously advancing DoD research priorities. The proposed acquisition operates as a user facility, with provisions to enhance access for other minority serving institutions (MSIs), notably our partners at University of Texas, El Paso.

The proposed facility will contribute to the research and development of next-generation materials for electronic devices, medical diagnostics, energy storage and harvesting, and surface protection that are relevant to the Army and DoD. Within the UCSB campus alone, impacted DoD-funded research ranges from basic (TLR 1) investigations of the optoelectronic properties new two-dimensional heterostructures to antireflective coatings undergoing testing in collaboration with ARL (TRL 5/6). Moreover, the facility will provide an important educational tool and training venue for undergraduate, graduate, and post-doctoral students through its incorporation into coursework on light-matter interactions and materials characterization. The facility will become part of the Materials Research Facilities Network (MRFN), a collaborative effort focused on increasing the visibility and usage of analytical and computational instrument centers. The MRFN particularly emphasizes access by MSI partners, with the purpose of attracting more students to graduate research and improving retention through access to state-oft-he-art facilities. MRFN users typically submit short proposals requesting access to instrumentation, techniques, and highly skilled staff. Undergraduates will be recruited through existing programs administered by the MRL. These programs target undergraduate students from underrepresented groups in STEM fields from various institutions (research/teaching universities, community colleges, and junior colleges) throughout California and the US.

**Accomplishments:** The main goals of the award have been accomplished in the reporting period, as detailed in the uploaded report. The facility has been assembled and qualified, and opened to both internal UCSB and external users.

**Training Opportunities:** The reporting period encompasses the design, purchase, and qualification of the tool. A handful of graduate and undergraduate students have used the tool during the qualification period, receiving training on optical alignment, spectroscopic characterization of materials, and data analysis. However, the bulk of the training opportunities will occur in the near future, as the tool is now open for general use both internal UCSB users as well as external users, including from our partner MSI institutions.

**Results Dissemination:** As the instrument has only recently become fully functional, there are no results to disseminate yet; however, the presence of the instrument is advertised among the the core facilities at the UCSB California NanoSystems Institute.

**Honors and Awards:** Nothing to Report

**Protocol Activity Status:**

**Technology Transfer:** Nothing to Report

**PARTICIPANTS:**

**Participant Type:** PD/PI
**Participant:** Andrea F Young
**Person Months Worked:** 1.00
**Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

**Participant Type:** Co PD/PI
**Participant:** Michael Gordon
**Person Months Worked:** 1.00
**Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

**Participant Type:** Technician
**Participant:** Lee Sawyer
**Person Months Worked:** 2.00
**Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

**RPPR Final Report**
as of 11-Feb-2019

## Facility implementation and description

UCSB has received and utilized an award dedicated to building UV/Vis/Raman spectroscopy and imaging instrumentation for chemical and structural characterization of materials. UCSB is both a major research university and Hispanic Serving Institution, providing a unique opportunity to leverage a well-developed infrastructure to expand minority access to cutting-edge instrumentation while simultaneously advancing DoD research priorities. In summary, over the 2 year course of the project, UCSB has successfully purchased and integrated all of the components needed for the instrument and qualified it. The instrument is now open for use to both internal and external users, including discounted or free use for users from other minority serving institutions.

The funded instrumentation operates as a user facility. The facility is a part of UCSB core research instrumentation, administered by the interdisciplinary campus center known as the California Nanosystems Institute. Detailed descriptions of the facility, sign up calendar (for registered users) and status updates are available through the core facilities website at

http://www.cnsi.ucsb.edu/resources/facilities/ncf/spectroscopy.

The current incarnation of the system—designed to be open plan and thus suitable to be upgraded as additional funds become available---includes the following specifications:

- Horiba Jobin Yvon T64000 open-frame confocal microscope with triple monochromator and LN2 cooled CCD array detector
    - Objectives: 10X, 50X, 50X ultra long working distance, 100X
    - Reflected light (spectroscopy) and Kohler illumination
    - Ultimate pixel resolution on sample @ 100X is ~300 nm
    - Stage scanning (150mm x 150mm)
    - Galvano-mirror DuoScan fast beam scanning
    - Objective turret attachment for spectroscopy of liquid samples in a cuvette
- Monochromator(640 mm focal length)
    - Single mode (150 & 1800 groove/mm gratings) for 360-950 nm
    - Ultra-high spectral resolution using triple additive /subtractive modes
    - LN2 cooled CCD array detector (1024 x 256 pixels)
    - Auxiliary photomultiplier and avalanche photodiode detectors
- Spectroscopy capabilities
    - Point scans and spatially correlated spectroscopic imaging
    - Raman and Photoluminescence spectroscopy
    - Raman pump line available @ 488 nm (457, 514, 532, 568, 647 nm coming soon)
    - Simultaneous Stokes and anti-Stokes Raman
    - Triple mono mode: within 5 cm-1 of Rayleigh line
- Excitation Sources
    - Mixed gas Ar/Kr ion laser @ 488 nm (457, 476, 488, 514, 527, 568, 647 nm)
- Sample Environments
    - Ambient stage
    - 2K-350K Cryostat
    - 300K-1200K Vacuum or gas flow heated stage

Materials research at UCSB is highly inter-disciplinary, relying on user facilities in the Materials Research Laboratory (MRL) and California NanoSystems Institute (CNSI) that together provide NMR, electron and scanning probe microscopy, x-ray characterization, and now optical spectroscopy. Shared facilities are critical to research and development across the campus and the region, much of which is DoD supported. Moreover, the high degree of accessibility makes UCSB shared facilities a hub for external users, including users from regional and national MSIs.

The proposed facility is already contributing, despite having been open to users for only a few short months, to the research and development of next-generation materials for electronic devices, medical diagnostics, energy storage and harvesting, and surface protection that are relevant to the Army and DoD. Within the UCSB campus alone, impacted DoD-funded research ranges from basic (TLR 1) investigations of the optoelectronic properties new two-dimensional heterostructures to antireflective coatings undergoing testing in collaboration with ARL (TRL 5/6). Moreover, the facility is setup to provide an important educational tool and training venue for undergraduate, graduate, and post-doctoral students through its incorporation into coursework on light-matter interactions and materials characterization, which is now in development.

Two science examples are listed below showcasing the research impact of the instrument on UCSB research. In addition, now that the instrument is open to users, we are working with our primary MSI partner (UT El Paso) to facilitate access both through student travel and by remote sample characterization to be carried out by technical staff and collaborators at UCSB.

## Example 1: Residual Stresses in Oxide turbine blade coatings

Important developments in turbine blade technology, including cast thin-walled airfoils with complex internal cooling passes, place significant thermal gradients and stresses on the multilayered coating systems used to thermally insulate the blade from the hot combustion gases. As gas turbine engine operating temperatures increase, the intermetallic bond coatings traditionally used in thermal barrier coating systems undergo increased creep deformation. Bond coats for single-crystal turbine blades have been designed primarily for oxidation protection with minimal consideration of mechanical and microstructural optimization. At higher temperatures, intrinsic failure mechanisms of coatings such as rumpling and cracking due to sustained peak low-cycle fatigue (SPLCF), limit the lifetimes of engine blades. Bond coatings have been shown to extend or reduce the SPLCF lifetime of a specimen as compared to uncoated single-crystals.

Optical spectroscopy enabled by the Horiba system have allowed investigation of the mechanical and microstructural properties of bond coatings and their oxides, both of which impact fatigue crack propagation rates. For example, the residual growth stresses/strains in a thermally grown oxide (TGO) at room temperature and the TGO growth strains at temperature are important driving forces for several failure mechanisms of thermal barrier coating systems. (1) The residual stresses at room temperature increase the driving force for spallation of the TGO (edge delamination). (2) The TGO growth strains at high temperature provide a driving force for oxide elongation, increasing rumpling rates. (3) The oxide growth strains increase the TGO penetration rate during SPLCF cycling leading to shorter fatigue lifetimes.

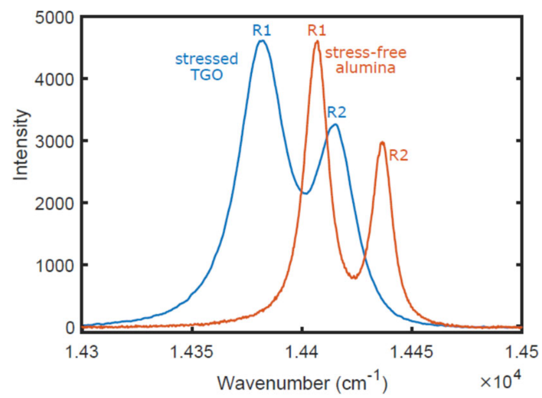


*Figure 1: Example of the peak shifts that occur between a stress-free alumina reference and a stressed TGO. The R1/R2 doublet shifts to lower wavenumbers for higher compressive stresses.*

The stress in the TGO at high temperature becomes a balance between the oxide growth rate, and the corresponding creep rate of the TGO. Growth strains/stresses have been measured via in-situ synchrotron techniques as well as via room temperature piezospectroscopy on both Ni-base single-crystal superalloys and bond coats. Photo-stimulated luminescence spectroscopy (PSLS) can be used at room temperature to measure peak shifts in the Cr3+ R-line doublet and to calculate the residual stress with the piezospectroscopic tensor. The Horiba spectroscopy system has been key to strain mapping of these stresses in Alumina thermal barrier coatings.

$Cr^{3+}$ dopant ions that are present in α-alumina TGOs fluoresce when excited by a laser, producing a characteristic R-line doublet (R1 and R2). Shifts in the α-alumina peak positions are sensitive to residual stresses in the scale (Figure 3). Unstressed α -alumina has an R2 peak around 14433 cm$^{-1}$ and an R1 peak around 14403 cm$^{-1}$. The doublet position is sensitive to stress, temperature, and Cr-content within the TGO. The Horiba

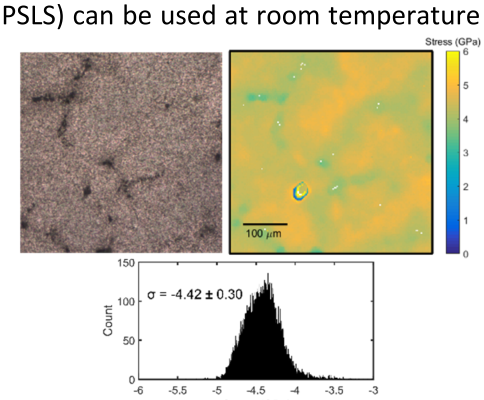


*Figure 2: Optical image and extracted stress profile of Single crystal Rene N5 TBC alloy materials. Lower panel: Stress distribution.*

system has allowed rapid spatial mapping of the corresponding stress, as shown in Figure 2, providing critical feedback into these technologically relevant materials.

## Example 2: Rhombohedrally stacked graphene for flat band engineering

Correlated electron physics holds the key to advanced electronic circuits based on new functionalities. A promising avenue is in moiré heterostructures of 2D materials, where an artificial superlattice arises from the interference of mismatched 2D crystal lattices. One intriguing proposal relies on interfaces between hexagonal boron nitride and rhombohedrally stacked three-layer graphene, and the Raman spectroscopy system has been key to enabling the creation of these devices.

Few layer graphene exhibits unique physical properties distinct from both monolayer graphene and graphite. Weak coupling between single graphene layers allows for multiple energetically stable stacking configurations, each with differing electronic properties. In trilayer graphene, ABA or Bernal stacking is the most energetically favorable and also the most studied. ABC-stacked trilayer graphene (ABC-TLG), which has rhombohedral symmetry, is also naturally present in exfoliated trilayer graphene, however, it is less energetically favorable and probe to relaxation, in the 2D limit, to the ABA structural ground state.

ABC-TLG hosts electronic bands which exhibit very weak dispersion near the charge neutrality point, making it a primising platform for studying the effects of electron interactions. In order to study the electronic properties of ABC-TLG in devices, we need to spatially resolve domains of ABC stacking in exfoliated graphene flakes in order to isolate them and include them in heterostructures. We use spatially-resolved Raman spectroscopy to map domains of different stacking configurations.

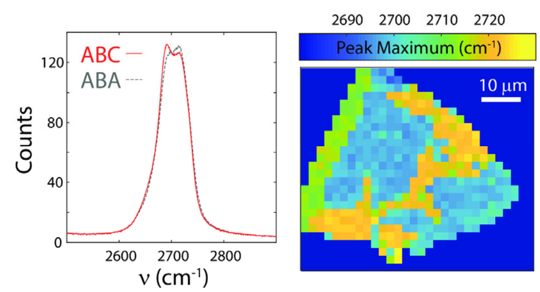


*Figure 3: Raman characterization of trilayer graphene stacking. (Left) The 2D-mode of trilayer graphene shows differences in peak shape when excited by 488 nm light. The 2D peak in ABC-stacked trilayer graphene (red solid line) exhibits a lower wavenumber maximum than the more common ABA-stacked version. (Right) A spatial map of the peak maxima observed by Raman spectroscopy on an exfoliated trilayer graphene flake. Large ABC domains (blue) are observed, but are separated by regions of ABA stacking (yellow).*

The Raman 2D (or G') mode of graphene is sensitive to both phonons and electronic structure, and its lineshape allows for discrimination between graphene with different numbers of layers and more relevantly stacking order[1]. Using the Horiba Raman system, we can quickly resolve the difference between ABA and ABC-TLG by the lineshape of the 2D mode, and efficiently map the stacking order of many flakes in order to find large enough ABC domains to make devices (Fig. Figure 3). ABC-TLG can revert to ABA stacking through accidental strain during device assembly, and Raman spectroscopy allows us to monitor the stacking order throughout our fabrication process.